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Synthesis, Physical and Chemical Properties, and Potential Applications of Graphite Fluoride Fibers

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Ching-cheh Hung
Lewis Research Center
Cleveland, Ohio

and

Martin Long and Mark Stahl
Cleveland State University
Cleveland, Ohio

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SYNTHESIS, PHYSICAL AND CHEMICAL PROPERTIES, AND POTENTIAL APPLICATIONS OF GRAPHITE FLUORIDE FIBERS

Ching-cheh Hung
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

and

Martin Long and Mark Stahl
Cleveland State University
Cleveland, Ohio 44115

SUMMARY

Graphite fluoride fibers can be produced by fluorinating pristine or intercalated graphite fibers. The higher the degree of graphitization of the fibers, the higher the temperature needed to reach the same degree of fluorination. In this study pitch based fibers were fluorinated to fluorine-to-carbon atom ratio between 0 and 1. The graphite fluoride fibers with a fluorine-to-carbon atom ratio near 1 have extensive visible structural damage. On the other hand, fluorination of fibers pretreated with bromine or fluorine and bromine result in fibers with a fluorine-to-carbon atom ratio nearly equal to 0.5 with no visible structural damage. The electrical resistivity of the fibers is dependent upon the fluorine to carbon atom ratio and ranged from 10^{-2} to 10^{11} Ω-cm. The thermal conductivity of these fibers ranged from 5 to 75 W/m-K, which is much larger than the thermal conductivity of glass (1.1 W/m-K), which is the regular filler in epoxy composites. If graphite fluoride fibers are used as a filler in epoxy or PTFE, the resulting composite may be a high thermal conductivity material with an electrical resistivity in either the insulator or semiconductor range. The electrically insulating product may provide heat transfer with lower temperature gradients than many current electrical insulators. Potential applications are presented.

E-3699

INTRODUCTION

Electrically-insulating engineering materials are generally also thermally insulating, which in many electrical systems is an important disadvantage. This is because the heat produced by the system is dissipated very slowly through the thermal insulator resulting in an accumulation of waste energy and requiring an increase in heat rejection temperature to maintain thermal equilibrium with the environment. Consequntly, degradation of electrical performance life and/or reliability of the system may result. State-of-the-art electrical systems, where higher power levels are being dissipated from smaller volumes, face such a thermal challenge. Examples of the insulators described above are: printed circuit boards for high density power electronics; insulators for windings of alternators; substrates for thin film resistors; and electrical protection layers in aircraft deicers. The deicer protection layers electrically protect the heating elements and their power sources from lightning strike, and at the same time transfer the heat from the heating element to the icing surface (ref. 1). Heat dissipation problems

may be alleviated by using graphite fluoride fibers developed in this study as a filler in epoxy or polytetrafluoroethylene (PTFE) to form a thermally conductive electrical insulator.

Graphite fluoride is most commonly produced by fluorinating graphite materials with fluorine gas at a high temperature. It is electrically insulating, chemically inert, and hydrophobic. Its molecular structure differs from that of graphite in that the unit cell has a cyclohexane, rather than a benzene, structure, with the fluorine atom bonded to the carbon atom covalently (fig. 1, ref. 2). Industrial applications for this material have been explored during the past two decades (ref. 3). Currently, it is commerically available in the powder form for use as a dry lubricant, or cathode material in lithum batteries. Reports of graphite fluoride in the fiber form are scarce. However, Endo recently reported that the ultrathin, highly graphitized vapor grown fibers can be fluorinated (ref. 4). Recently graphite fluoride was also produced by reacting fluorine with intercalated graphite materials[1] at high temperature (refs. 3 and 5).

The thermal conductivity of graphite fluoride has not been explored previously. However, the value is likely to be high if the damage to the carbon-carbon bonds during the fluorination reaction is small. This is because the major mechanism for thermal conduction at room temperature is the transmission of moleular vibration through the covalent carbon-carbon bonds. Molecular vibration transmission via the carbon-carbon double bonds in graphite single crystals and the high modulus P-100 graphite fibers from Amoco produces a thermal conductivity four times that of copper (i.e., 1600 W/m-K, ref. 6) and comparable to copper (i.e., 300 to 520 K, refs. 7 and 8), respectively.

In this study, graphite fluoride in fiber form was synthesized and characterized. The thermal conductivity and electrical resistivity of graphite fluoride fibers was measured. Potential applications of this new material suggested by the results of this report is also discussed.

METHODS AND EXPERIMENTS

Graphite Fibers

Two highly graphitized pitch fibers (P-100 and P-75) and two less graphitized pitch fibers (P-55 and P-25) from Amoco Corporation were used in this study. In addition to pristine fibers, high temperature fluorination of fibers preintercalated with fluorine and copper fluoride was studied in order to understand the effect of fluorine intercalation on the subsequent high temperature fluorination reaction. Also studied were high temperature fluorination of P-100 and P-75 fibers pretreated with bromine at room temperature, and high temperature fluorination of P-55 fibers pretreated sequentially with fluorine and bromine at room temperature. The brominated P-55 fibers describe above were preintercalated with fluorine because bromine does not react with pristine P-55, but does react with fluorine intercalated P-55. Intercalation

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[1]Intercalation is a process in which guest atoms or molecules are inserted into the space between the graphite layers.

of these pitch fibers with fluorine and bromine is described in detail elsewhere (refs. 9 and 10).

In order to understand the reaction between fluorine and PAN fibers, one PAN fiber sample, Amoco's T-300, was also tested for fluorination reaction.

Fluorination Reactions

Approximately 0.3 gram of each fiber described above was placed in a crucible for fluorination. The crucible containing the fiber was placed in a 61 cm long, flanged, 3-in. Schedule 40 nickel pipe which was connected to the gas source. The outlet of this fluorination reactor was connected to a bed of aluminum oxide beads where the fluorine was reduced to aluminum fluoride. All materials were made of nickel except for the crucible stand and the gas inlet tube, which were made of copper. This system was purged with nitrogen and heated for 2 to 3 hr before fluorine was introduced into the pipe at a controlled flow rate. Fiber fluorination was conducted in the temperature range of 250 to 550 °C. Pure fluorine at 1 atm pressure was used in all experiments except one, where in order to study fluorine partial pressure effects, a mixture of 1 percent fluorine and 99 percent nitrogen was used to fluorinate pristine and brominated P-75 at 390 °C. The reaction time was 21 hr unless otherwise specified. The fluorine flow rate was 50 cc/min during the first 2 to 3 hr of fluorination, and 25 cc thereafter. After fluorination, the system was cooled and purged with nitrogen.

Microscopic Examination

All graphite fluoride fibers were examined under an optical microscope with 19 - 390X magnificiation. The fiber structural damage which occurred during fluorination was examined. Also, assuming the fiber diameter was 10 μm before fluorination, the diameter changes during fluorination were measured.

Weight Analysis

The weights of all fiber samples before and after fluorination were measured. Knowing that the weight of bromine in brominated fiber samples is 18 percent of The carbon weight before fluorination (ref. 9), and assuming no bromine loss during fluorination, the weight gains thus obtained were then used to calculate the fluorine content in the fiber.

Electrical Resistivity

For most samples the two point method was used to measure the resistivity. In this method both ends of the single fiber or fiber strands were painted with either carbon or silver paint to form the electrical contact to an ohmmeter. The electrical resistivity is equal to the measured fiber resistance times the fiber cross-sectional area and then divided by the fiber length. The four-point method (ref. 9) was used only in cases where the fiber resistance values were so small that they were comparable to the contact resistance between the fibers and the paints.

Thermal Conductivity

Nine or 16 strands of fibers were embedded in an epoxy block to form a sample. The thermal conductivity of the fibers was calculated by excluding the epoxy contribution from the thermal conductivity of the fiber-epoxy composite samples. Details of this calculation and the thermal conductivity measurement method were described previously (ref. 7). Because of the time consuming nature of such a study, the thermal conductivities of only selected samples were measured. The samples were selected based on either the significance of the experimental data or the importance for potential industrial applications.

RESULTS AND DISCUSSION

Visual and Microscopic Observation

Figure 2 is a photograph of one graphite fiber sample and six graphite fluoride fiber samples. The six graphite fluoride fiber samples were produced by fluorinating pristine P-100, P-75, P-55, T-300, and brominated P-100, and P-75 fibers, at 450 °C for 21 hr. Figure 3 contains microphotographs of the graphite fluoride fibers described above. Structural damage during fluorination can be observed on fibers produced from pristine graphite, but not on those produced from brominated graphite. Figure 3 also includes a graphite fluoride fiber produced from a fluorine intercalated fiber. This fiber sustained observable structural damage, but was not as extensively damaged as those produced from pristine fibers. This indicates that both bromine and fluorine intercalated in the fibers modify the kinetics of fluorination. However, in order to obtain graphite fluoride fibers with the least structural damage, brominated fibers are preferred over fluorine intercalated fibers or pristine fibers as a raw material.

Graphite fluoride fiber samples with high fluorine content and produced from brominated graphite fibers are dark yellow in color. This is different from the typical white, grey, or black color of graphite fluoride. It is an indication that some bromine exists in this product.

Fluorination of PAN based T-300 resulted in extremely fragile fibers, and was not investigated further.

Weight Analysis

Tables I and II show the composition of graphite fluoride fibers produced from fluorinating pristine and intercalated graphite fibers, respectively, for 21 hr unless otherwise specified. From these two tables, the relative reactivity of pristine and intercalated fibers to fluorine gas can be observed. Pristine fibers react with fluorine gas at a relatively high temperature. This reaction produces graphite fluoride with a fluorine-to-carbon atom ratio equal or close to 1.0. Brominated fibers, on the other hand, react with fluorine gas at a relatively low temperature, producing graphite fluoride with a fluorine-to-carbon atomic ratio equal to 0.5. However, fluorination of brominated fibers will not increase the fluorine to carbon atom ratio to much more than 0.5 unless the fluorination temperature is extremely high (550 °C). These data suggest that bromine acts as a catalyst to initiate the fluorination

reaction, producing a stable compound which resists further fluorination. Such a compound may be similar to the C_2F suggested by Nakajima and Watanabe (refs. 3 and 5), but is believed to contain bromine.

Tables I and II also indicate that the higher the degree of graphitization of the fibers, the higher the temperature needed to reach the same degree of fluorination.

As shown in table II, the fluorine intercalated and then brominated P-55 fibers were subsequently treated with fluorine by three different reaction time and temperature combinations. The purpose of these three experiments was to produce graphite fluoride fibers of the same composition by fluorinating the same fibers for different duration and temperature combinations. Only two of these experiments, i.e., 350 °C for 4 hr and 300 °C for 21 hr, resulted in fibers with the same composition. The high-temperature, short-time experiment resulted in fibers with extensive visible structural damage, but the low-temperature, long-time experiment produced fibers with no visible structural damage. The third experiment, i.e., 275 °C for 48 hr, produced fibers with a different composition than that of the other two samples ($CF_{0.39}Br_{0.026}$). However, to the best knowledge of the authors, the fluorination temperature used in this experiment, 275 °C, is the lowest fluorination temperature ever reported.

The results described above seem to suggest that slow fluorination can reduce fiber structural damage. However, this is not always the case. It is noted that a fluorination reaction at 450 °C for 21 hr in a mixture of fluorine at 0.01 atm and nitrogen at 0.99 atm caused more damage to pristine and brominated P-75 than reaction at 450 °C and 21 hr in fluorine at 1 atm did, even though the former reaction is presumably slower due to the low partial pressure of fluorine. The relation between fluorination kinetics and the structural damage is evidently too complex to be determined by the experiments described here.

Electrical Resistivity

Table III shows the electrical resistivity of the graphite fluoride fibers and the standard deviation from the average of 5 or 6 values. The fluorine-to-carbon atom ratio is also included in this table for comparison. For the sake of simplicity, only the most representative data are shown in this table. It can be seen that the resistivity of the fibers can be tailored to meet the values required for certain applications. Also, in comparing the weight data to electrical conductivity data, several phenomena can be observed.

The standard deviation as a percentage of the average resistivity value reaches a maminum when the fluorine-to-carbon atom ratio is about 0.5. This suggests that the environment for the conduction electrons changes significantly when the fluorine-to-carbon atom ratio changes from slightly smaller to slightly larger than 0.5. The electrical resistivities are in semiconductor range at this fluorine fraction.

The electrical resistivity of graphite fluoride fibers was found to be closely related to the fluorine-to-carbon atom ratio.

When the fiber has a fluorine-to-carbon atom ratio near zero, the fluorinated fiber is a conductor, which has a detectable electrical resistivity change from the pristine value even though the existance of fluorine cannot be detected.

With one exception (the only experiment in this study where fluorination reaction was completed in a short time, i.e., 4 hr), when the fiber has a fluorine to carbon atom ratio near 0.5, it remains free of visible structural damage when examined under an optical microscope, with electrical resistivity in either semiconductor or insulator range, i.e., from 0.01 to higher than 10^{11} Ωcm.

When the fiber has fluorine-to-carbon atom ratio near 1.0, structural damage to the fibers is always visible under an optical microscope, and it is an insulator, with electrical conductivity too low to be measured accurately.

Products without structural damage, and with fluorine to carbon ratios near 0.5 are most useful for industrial applications. In this project, they were produced only by fluorinating fibers pretreated with bromine. Some fibers of this type were selected for thermal conductivity testing.

Thermal Conductivity

Table IV summarizes the thermal conductivity values of selected samples. Electrical resistivity and fluorine to carbon atom ratio of these samples are also shown in this table in order to examine (1) their relations to the thermal conductivity of these samples, and (2) the possible applications requiring a certain combination of electrical and thermal properties. The graphite fluoride fibers produced from fluorinating prebrominated P-75 at 370 or 390 °C for 21 hr are electrical insulators having thermal conductivites (5 and 10 W/m-K) much higher than ordinary glass (1.1 W/m-K) or quartz (1.4 W/m-K). Epoxy or PTFE composites made with this fiber could be used to replace fiber glass-epoxy or quartz-epoxy composites in applications where high thermal conductivity would improve the performance, such as printed circuit board-heat sinks, electrical insulator-heat sinks for the windings in an electric generator, substrates material for thin film resistors, or electrical protection layers in an aircraft deicer. The graphite fluoride fibers produced by fluorinating prebrominated P-100 at 350 and 370 °C for 21 hr have electrical resistivity in semiconductor range and thermal conductivites (50 and 75 W/m-K) comparable to iron (75 W/m-K). The graphite fluoride fiber produced by fluorinating P-55 fibers pretreated with both fluorine and bromine at 300 °C for 21 hr also has electrical resistivity in semiconductor range. Its thermal conductivity (20 W/m-K) is comparable to stainless steel (15 W/m-K). The last fiber material described above is much less expensive than the other fiber materials, and therefore may be more attractive for potential industrial application. The last three fibers described above may be useful as a material for making resistors. They also may provide an improved cathode material for lithum batteries. Due to the fibrous shape of the graphite fluoride, the cathode material thus made is more electrically and thermally conductive than that made from powdered graphite fluoride with comparable fluorine content. Therefore, electrical conductivity enhancement chemicals may not be needed to form a conductive cathode, and this may allow the lithum battery to operate at higher current without causing overheating.

CONCLUSION

Fluorinating pristine or intercalated pitch fibers at high temperatures can result in graphite fluoride fibers. The higher the degree of graphitization of the fibers, the higher the temperature needed to reach the same degree of fluorination.

After fluorinating the pristine graphite fibers, the fluorine-to-carbon atom ratio in the product can be between zero and 1.0. For these two extremes, the fluorination temperatures are 350 and 450 °C, respectively, for most graphitized P-100, and 250 and 350 °C, respectively, for nongraphitized P-25.

Unlike pristine fibers, fluroination of brominated fibers results in fibers with a fluorine-to-carbon atom ratio nearly equal to 0.5 and with no visible structural damage. The electrical resistivities of the fibers measured in this study were either in the semiconductor range, from 10^{-2} to 10^{6} Ω-cm, or in the insulator range, larger than 10^{11} Ω-cm. The thermal conductivity of these fibers was in the 5 to 75 W/m-K range, which is much larger than that of glass or quartz (1.1 and 1.3 W/m-K, respectively), which is the regular filler for epoxy. Therefore, graphite fluoride fiber-epoxy composites may have application where heat dissipation is important, such as printed circuit boards in high density power electronics, insulators in the windings of alternators, substrates material in thin film resistors, and the protection layers in aircraft deicers. Also the graphite fluoride fibers with electrical resistivity in semiconductor range could be used as an improved heat sink-cathode material in high power lithum batteries.

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TABLE I. - FLUORINE TO CARBON ATOM RATIO IN GRAPHITE FLUORIDE FIBERS PRODUCED BY FLUORINATING PRISTINE PITCH BASED GRAPHITE FIBERS AT A FLUORINE PRESSURE OF 1 ATM FOR A HEATING TIME OF 21 HR UNLESS OTHERWISE SPECIFIED.

Temperature, °C	P-100	P-75	P-55	P-25
450	0.84	0.89	1.0	-----
450	----	[a].7?	---	-----
390	[b].66	.79	---	-----
350	.024	-----	0	0.91
300	0	-----	0	-----
250	0	-----	0	0.004
Room temperature	[c]0	-----	---	-----

[a]Fluorinated in a mixture of 1 percent florine and 99 percent nitrogen.
[b]The sample size was 10 gm, all other samples were 0.3±0.05 gm, heating sequence was: 15 hr at room temperature, 6 hr at 200 °C, ramp at constant rate over 36 hr to 390 °C, then 6 hr at 390 °C.
[c]1 hr of fluorination.

TABLE II. - FLUORINE TO CARBON ATOM RATIO IN GRAPHITE FLUORIDE FIBERS PRODUCED BY FLUORINATING BROMINE INTERCALATED PITCH BASED GRAPHITE FIBERS AT A FLUORINE PRESSURE OF 1 ATM FOR A HEATING TIME OF 21 HOURS, UNLESS OTHERWISE SPECIFIED.

Temperature, °C	P-100 ($CBr_{0.026}$)	P-75 ($CBr_{0.026}$)	P-55[a] ($CF_{0.07}Br_{0.026}$)
500	0.75	0.79	-----
450	.65	.66	-----
450	----	[b].70	-----
390	[c].49	.62	-----
370	.50	.57	-----
350	.47	----	[d]0.53
300	.058	----	.54
275	-----	----	[e].39
250	0	----	-----
Room temperature	[f].099	----	-----

[a]The P-55 fibers were intercalated with copper fluoride and fluorine at room temperature, brominated, and reacted with fluorine at room temperature before high temperature fluorination.
[b]Fluorinated in a mixture of 1 percent fluorine and 99 percent nitrogen.
[c]The sample size was 10 gm, all other smples were 0.3±0.05 gm heating histogram was room temperature for 15 hr, then 200° for 6 hr, then increase to 390 °C at constant rate in 36 hr, then 390 °C for 6 hr.
[d]4 hr of fluorination.
[e]48 hr of fluorination.
[f]1 hr of fluorination.

TABLE III. - ELECTRICAL RESISTIVITY OF FIBERS PRODUCED BY FLUORINATING PITCH BASED GRAPHITE FIBERS AT A FLUORINE PRESSURE OF 1 ATM FOR A HEATING TIEM OF 21 HR UNLESS OTHERWISE SPECIFIED.

Fiber type	Fluorination temperature, °C	Electrical resistivity		Fluorine to carbon atom ratio
		Average, Ω-cm	Standard deviation, percent of average value	
P-100	none	2.53×10^{-4}	11.1	0
P-100	250	3.24×10^{-4}	7.41	↓
P-100	300	3.45×10^{-4}	4.93	↓
Br-P-100[a]	none	$.52\times10^{-4}$	9.62	↓
Br-P-100	250	$.76\times10^{-4}$	9.21	↓
Br-P-100	350	3.78×10^{-2}	17.7	0.47
Br-P-100	370	5.29×10^{2}	119	.50
Br-P-75	none	1.08×10^{-4}	8.33	0
Br-P-75	370	3.81×10^{6}	------	.57
Br-P-75	390	$>10^{11}$	------	.62
P-55	none	9.28×10^{-4}	15.6	0
P-55	250	8.32×10^{-4}	4.81	0
P-55	350	9.76×10^{-4}	12.4	0
F-Br-F-P-55[b]	300	$.21\times10^{4}$	28.6	.54
F-Br-F-P-55	[c]350	1.72×10^{4}	65.7	.53
F-Br-F-P-55	[d]275	3.2	43.8	.39

[a]The "Br-" indicates the fibers were prebrominated at room temperature.
[b]The F-Br-F indicates the fibers were intercalated with fluorine and copper fluoride, then brominated, and then reacted wtih fluorine gas at room temperature for 1 hr before the fluorination reaction.
[c]Fluorinated for 4 hr.
[d]Fluorinated for 48 hr.

TABLE IV. - THERMAL CONDUCTIVITY OF GRAPHITE FLUORIDE FIBERS PRODUCED BY FLUORINATING PITCH BASED GRAPHITE FIBERS AT A FLUORINE PRESSURE OF 1 ATM FOR A HEATING TIME OF 21 HR, UNLESS OTHERWISE SPECIFIED.

Fiber type	Fluorination temperature,	Thermal conductivity, W/m-K	Electrical resistivity, Ω-cm	Fluorine to carbon atom ratio
Br-P-75	370	10	3.81×10^{6}	0.57
Br-P-75	390	5	$>10^{11}$	.62
Br-P-100[a]	350	75	3.78×10^{-2}	.47
Br-P-100	370	50	5.29×10^{2}	.50
F-Br-F-P-55[b]	300	20	$.21\times10^{4}$	.54
Iron	room	75	---------	----
Stainless steel	room	15	---------	----
Quartz	room	1.3	---------	----
Glass	room	1.1	---------	----

[a]The "Br-" indicates the fibers were prebrominated at room temperature.
[b]The F-Br-F indicates the fibers were intercalated with fluorine and copper fluoride, then brominated, and then reacted with fluorine gas at room temperature for 1 hr before the fluorination reaction.

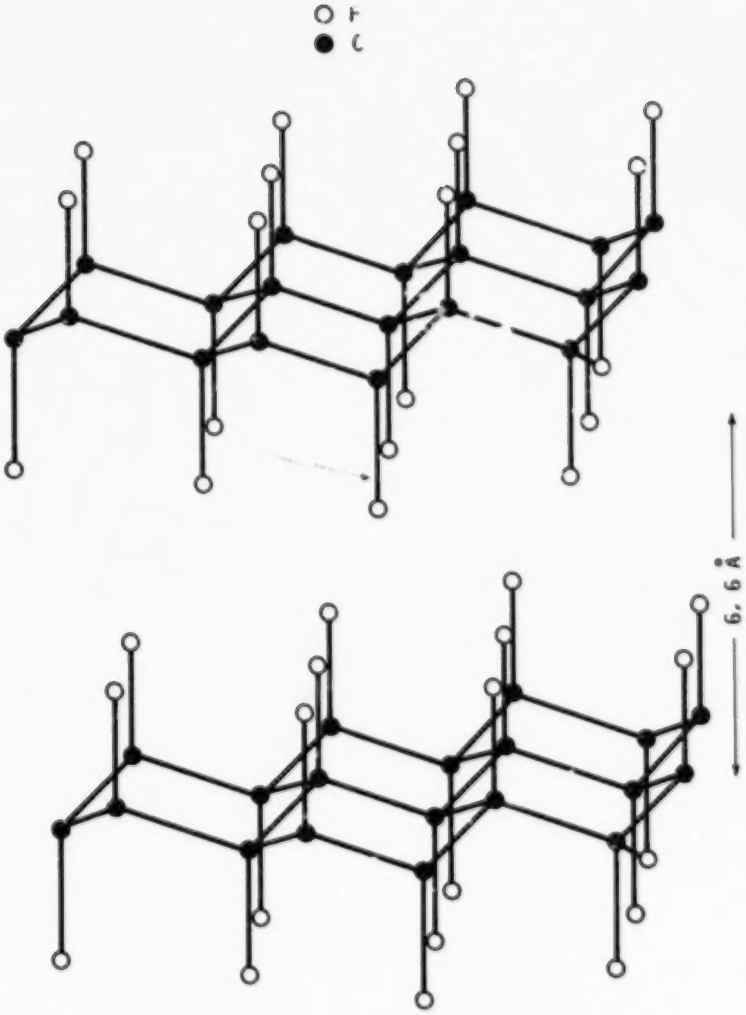

FIGURE 1. - MOLECULAR STRUCTURE OF GRAPHITE FLUORIDE $(CF)_N$.

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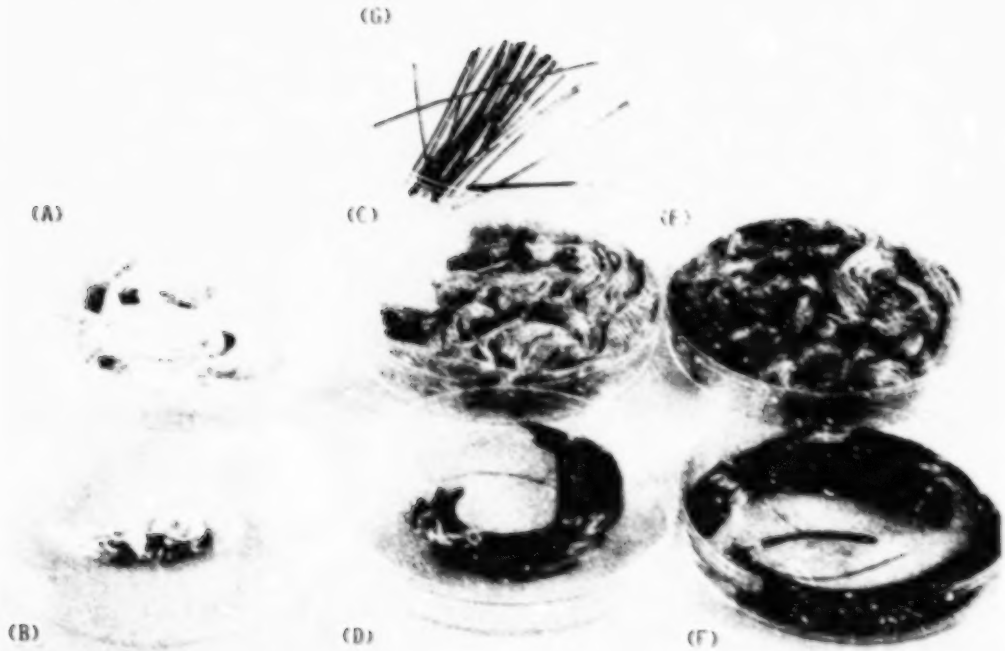

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FIGURE 2. - GRAPHITE FIBERS BEFORE AND AFTER FLUORINATION AT 1 atm BY FLUORINE GAS AT 450 ^{0}C FOR 21 HR. (A) P-55. (B) T-300. (C) P-75. (D) BROMINATED P-75. (E) P-100. (F) BROMINATED P-100. (G) TYPICAL PRISTINE GRAPHITE FIBER.

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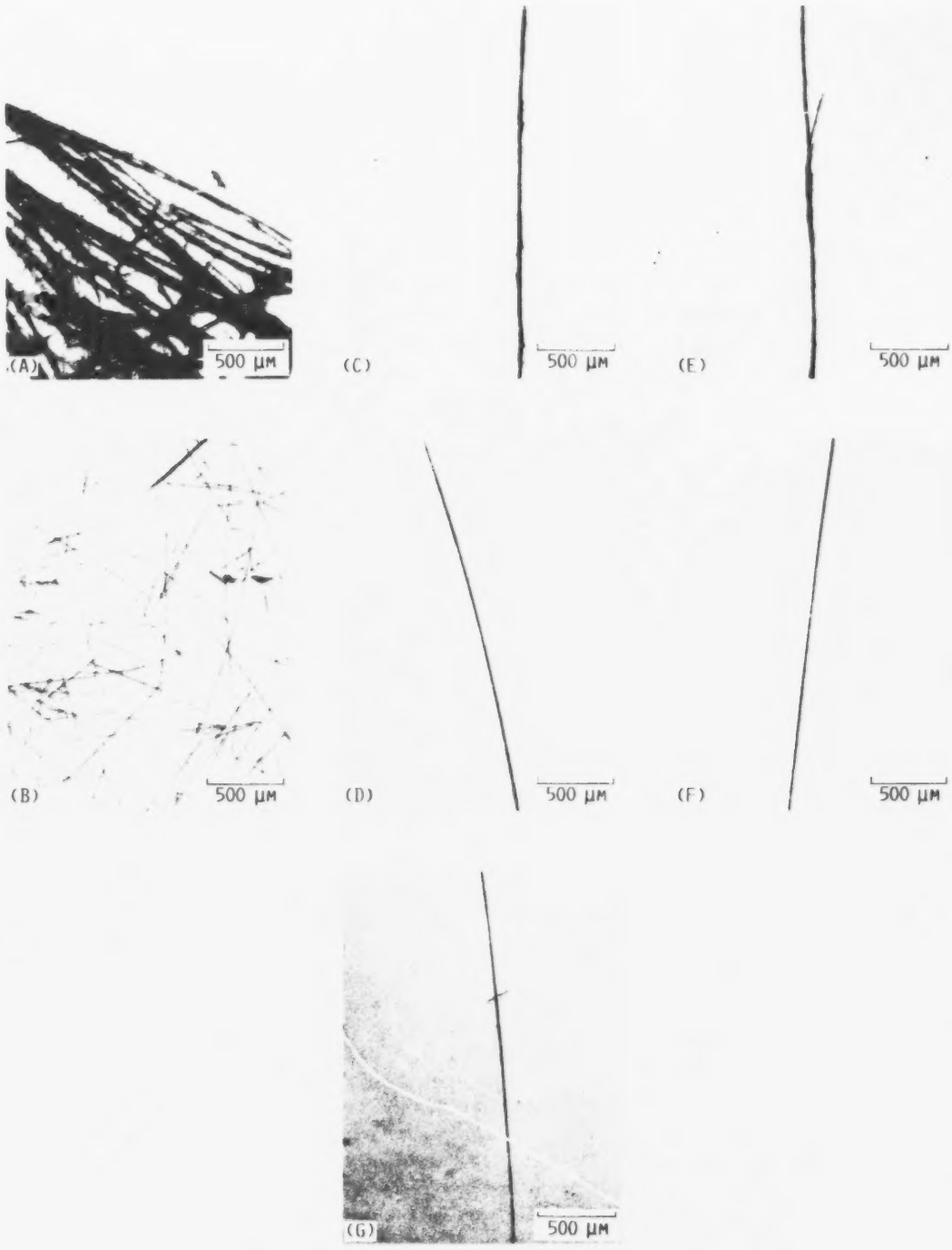

FIGURE 3. - MICROGRAPH OF GRAPHITE FIBERS AFTER FLUORINATION AT 1 ATM BY FLUORINE GAS AT 450 ^{0}C FOR 21 HR. (A) P-55, (B) T-300, (C) P-75, (D) BROMINATED P-75, (E) P-100, (F) BROMINATED P-100, (G) FLUORINE INTERCALATED P-75.

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16. Abstract
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